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Energy transfer dynamics in wire-type dendrimers having oligophenylene peripheries

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Abstract

Energy transfer and shielding effect are studied in wire-type dendrimers (G_n PPV: n -th generation dendrimer with poly(p -phenylenevinylene) backbone; $n = 1, 2$) having oligophenylene light-harvesting (LH) antenna. Following the excitation of the LH-antennae, backbone-polymers in G_n PPV give rise to intense photoluminescence (PL) bands. This is due to the presence of highly efficient energy transfer from the LH-antennae to the backbone-polymers. The intensity of backbone-PL increases faster than the decay of the antenna-PL. This result indicates that rapid energy-transfer from antenna to backbone takes place utilizing the overlap of wavefunctions in the excited states. In G_2 PPV having larger LH-antenna, shielding effect against inter-backbone interactions is recognized more effectively than G_1 PPV. In solid films of G_n PPV, red shifts of the backbone-PL bands are observed. This is caused by inter-backbone interactions of the wire-type dendrimers due to aggregation. The extent of the red shift in G_2 PPV is smaller than that of G_1 PPV. This result suggests that the larger LH-antenna in G_2 PPV substantially wraps its backbone-polymer and shields the inter-backbone interactions.

Keywords

Wire-type dendrimer, Light harvesting, Rapid energy transfer, poly- p -phenylenevinylene, oligophenylene,

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Introduction

Wire-type dendrimers have attracted much attention because they are promising materials for bright light emission [1]. In these dendrimers [1], backbone polymers were wrapped with large dendrons. In their solid films, the backbones were shielded by these dendrons against inter-backbone interactions. These interactions cause unnecessary energy dissipation, and hence result in the loss of light emission. In the previous studies, we have found that highly efficient and rapid energy transfer from the light-harvesting (LH) antenna to the porphyrin-core occurs in small dendrimers [2]. These small dendrimers have *meta*-branching oligophenylene as their LH-antenna. In these small dendrimers, since the aromatic rings in the LH-antenna are connected directly to the porphyrin-core, overlap of wavefunctions between their excited states is responsible for the rapid transfer [2].

In this study, we investigate the energy transfer and the shielding effect in wire-type dendrimers G_n PPV ($n = 1, 2$) having a poly(*p*-phenylenevinylene) (PPV) backbone. This backbone is wrapped with the LH-antenna of *meta*-branching oligophenylene.

Experimental

Chemical structures of G_n PPVs and their LH-antenna component molecules G_n TMSs are shown in Fig. 1. The polymerization degree m of backbone-PPV is ~ 100 and ~ 200 for G_1 PPV and G_2 PPV, respectively. Two types of samples were prepared. One is the tetrahydrofuran solution (10^{-5} - 10^{-6} M) of G_n PPVs, and the other is solid casting film of

*Gn*PPVs on quartz substrates. The second harmonic generation (SHG) output (~ 4.8 eV) of an optical parametric oscillation laser was used as a light source for time-integrated photoluminescence (PL) measurements. In time-resolved PL experiments, the samples were excited with a SHG output (~ 4.8 eV, ~ 100 fs pulse duration) of an OPA system pumped by a Ti:sapphire regenerative amplifier system. All measurements were performed at room temperature.

Results and Discussion

PPVs provide bright PL and electroluminescence [3]. However, inter-polymer interactions due to aggregations suppress their highly luminescent properties in solid films [4]. In *Gn*PPVs, it is expected that bulky LH-antennae protect backbone-PPV from the inter-backbone interactions.

In *Gn*PPVs, highly efficient energy transfer from the antenna to the backbone-PPV occurs. Figure 2 shows optical spectra of *Gn*PPV (solid line) and *Gn*TMS (broken line). Absorption bands of the LH-antenna and the backbone-PPV appear in the UV and visible light region, respectively. Under the excitation on the LH-antenna absorption band (4.8 eV: vertical broken line in Fig. 2), intense PL bands appear in *Gn*TMSs as indicated by light-gray shaded spectra in Fig. 2. On the other hand, in *Gn*PPVs, intense PL bands of the backbone-PPV are observed as indicated by dark-gray shaded spectra. The suppression of the antenna-PL and the appearance of the backbone-PL shown in Fig. 2 demonstrate that the

light energy absorbed in the LH-antenna is transferred efficiently to the backbone-PPV.

Based on the temporal response of the backbone-PL and the antenna-PL, we can conclude that rapid transfer takes place in *GnPPV*. In other dendrimers having LH-antennae constituted with non- π conjugated methylether-linkages ($-\text{OCH}_2-$) [1], Förster mechanism is applied to interpret the energy transfer from the relaxed luminescent states of the antenna to core. In this case, on account of the interactions between the transition dipoles of antenna-PL and core-absorption, the decay time constant τ_{ant} of the antenna-PL becomes shorter when compared to the case that the energy-transfer does not occur. Furthermore, the core-PL intensity shows a rise component of the same time constant with τ_{ant} . In contrast, the backbone-PL intensity of *GnPPV* shows faster rise than τ_{ant} . Figure 3(a) and 3(b) show the PL decay profile of the backbone-PPV (2.2~2.7 eV in Fig. 2) and the LH-antenna (3.2~4.0 eV in Fig. 2) in *G2PPV*, respectively. The decay profile of the antenna-PL has fast and slow decay components (broken-lines in Fig. 3(b)). Their origins can be readily assigned from the time-resolved PL spectra in the antenna-PL energy region in Fig. 3(d). A time-integrated PL spectrum of *G2TMS* is also shown in Fig. 3(e) as a reference. Based on the comparison of these set of time-resolved spectra, it is clear that the fast and slow decay components are, respectively, ascribable to the spectral overlap of the fast decaying backbone-PL (Fig. 3(a)) and the antenna-PL having the same decay time constant with *G2TMS* (Fig. 3 (c)). This result indicates that rapid transfer takes place from the antenna to the backbone-PPV in *G2PPV*, and its mechanism cannot be simply explained in terms of

Förster-type transfer. It should be interpreted as a sort of internal conversion-like process from the photo-excited states of the LH-antenna to the excited state of backbone-PPV.

Finally, we discuss shielding effects of the LH-antenna in *Gn*PPV. In solid polymer films, it is well known that the aggregation of polymers causes inter-polymer interactions. These interactions suppress the PL efficiency, and at the same time induce the polymer-to-polymer energy migration toward the lower energy sites [5]. In solid films of G1PPV, an obvious red-shift of the backbone-PL is observed in the time-resolved spectrum at $t \sim 0$ ns as shown in Fig. 4 (b) (compare the solution sample case in Fig. 4(a)). Temporal changes of the central energy of the spectral moment of the backbone-PL of G1PPV (closed triangles) and G2PPV (closed square) films are shown in Fig. 4 (c). Those of the solution samples are plotted with open marks in Fig. 4(c) for comparison. The extent of red-shift becomes large with the time course. However, the speed of the red-shift in G2PPV is somewhat slower than that in G1PPV. Also the extent of the red-shift in G2PPV is smaller than that in G1PPV. These results are good indication that the larger antenna in G2PPV shields inter-backbone interactions more effectively than in the case of G1PPV. Therefore, it is concluded that the wire-type dendrimer G2PPV having the large LH-antenna has suitable properties for a highly efficient light emitting material.

Summary

Rapid energy transfer from the LH-antenna to the backbone-PPV as well as a shielding

effect was investigated in the wire-type dendrimers G_n PPV. Upon the photo-excitation on the LH-antenna, the intense backbone-PL in G_n PPV shows faster rise than the decay of the antenna-PL reflecting the rapid energy-transfer process. In solid films of G_n PPV, red shifts of the backbone-PL due to the inter-backbone migration are observed. However, in G_2 PPV having large antenna, the red shift is smaller than that of G_1 PPV. It is suggested that the larger antenna in G_2 PPV shields the inter-backbone interaction effectively in its solid film.

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Fig. 1

Chemical structures of G_n PPV and G_n TMS ($n=1,2$). m is the polymerization degree of backbone-polymer in G_n PPV; $m \sim 100$ for G1PPV and $m \sim 200$ for G2PPV. TMS in G_n TMS means trimethylsilyl group.

Fig. 2

Absorption and PL spectra of G_n PPVs and G_n TMSs in solutions. PL spectra are displayed with grayish shadow. Vertical broken line marks the energy of the excitation.

Fig. 3

PL decay profiles of (a) the backbone-PPV and (b) the LH-antenna in G2PPV and (c) G2TMS. (d) Time-resolved PL spectra in the antenna-PL energy region of G2PPV. (e) Time-integrated PL spectrum of G2TMS.

Fig. 4

(a) Backbone-PL spectrum of G1PPV in solutions. (b) Time-resolved backbone-PL spectrum of the G1PPV film at $t \sim 0$ ns. (c) Solid marks indicate the temporal changes of the central energy of core-PL spectral moments in G_n PPV films. Open marks denote those of the time-integrated backbone-PL in solutions.

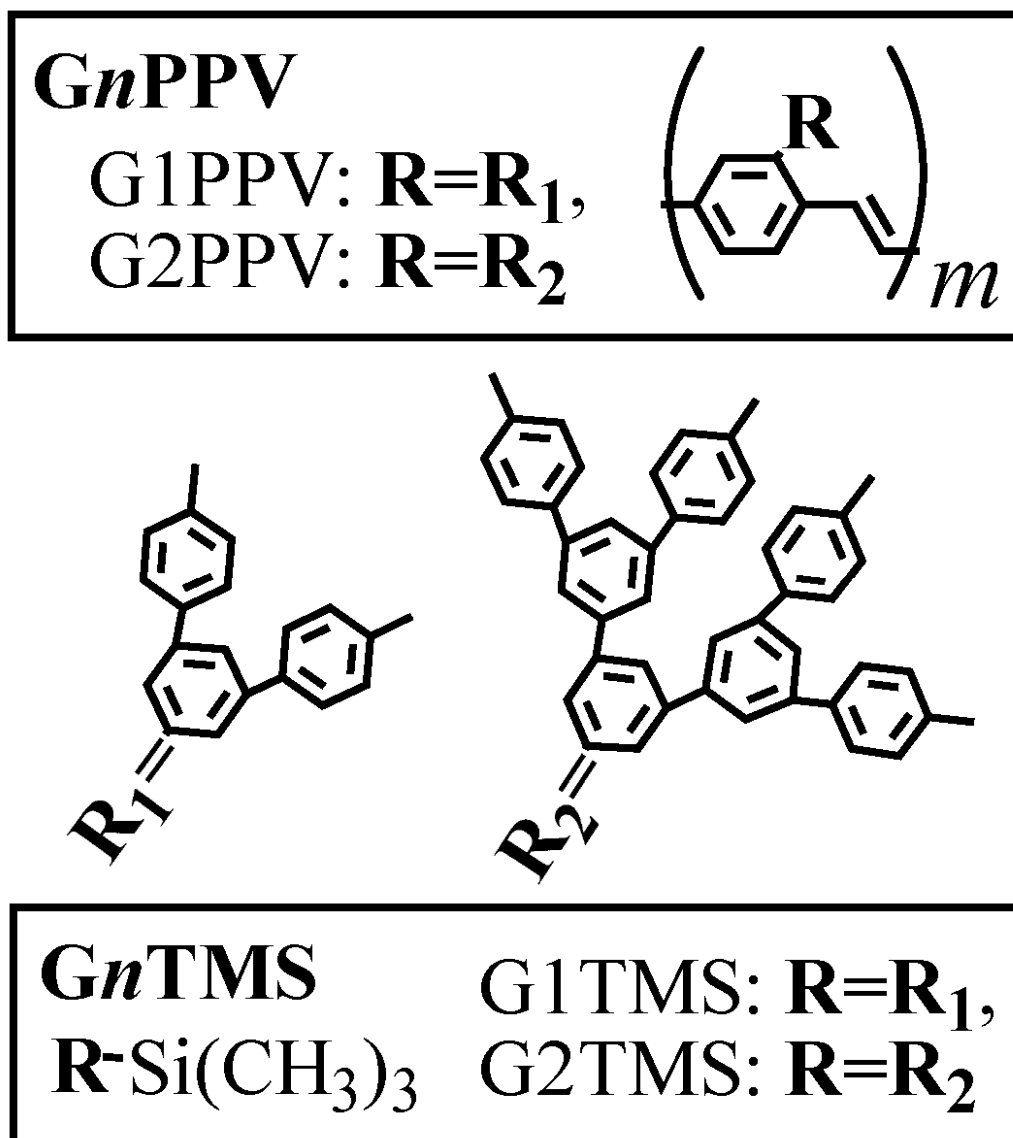


Fig.1

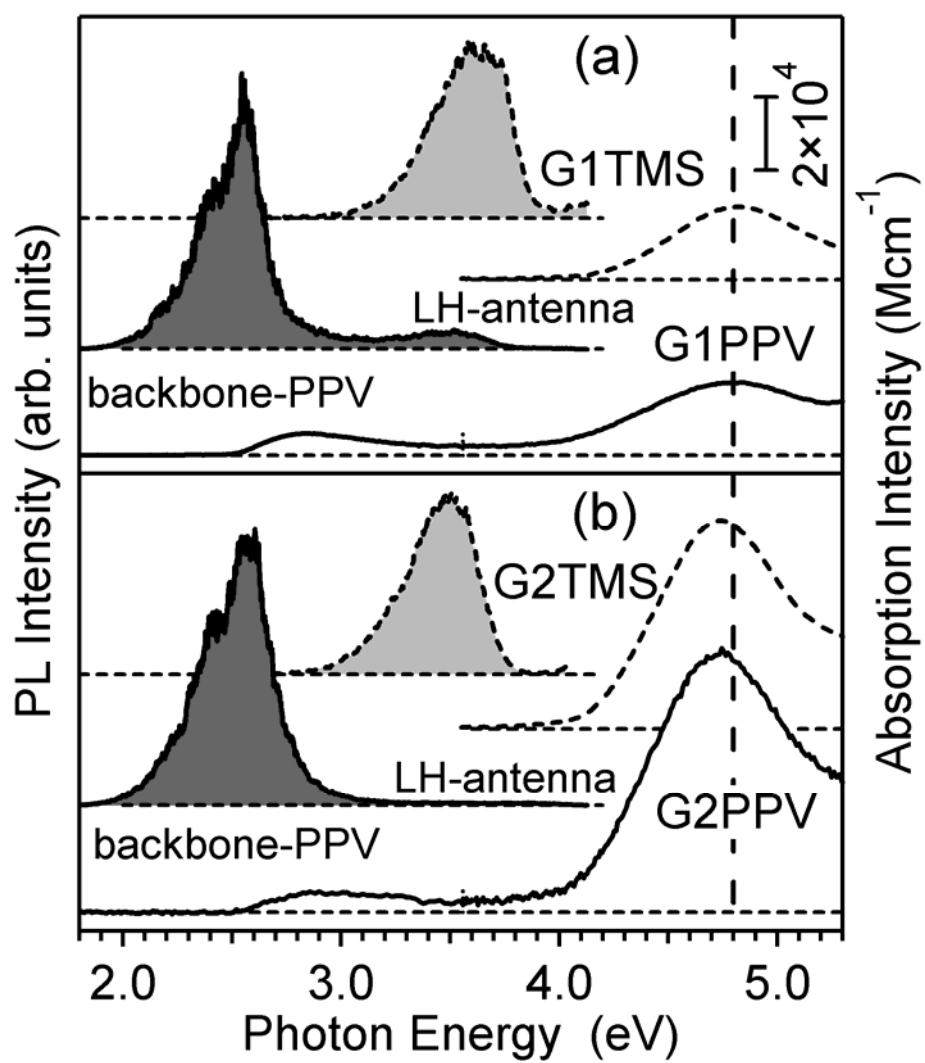


Fig.2

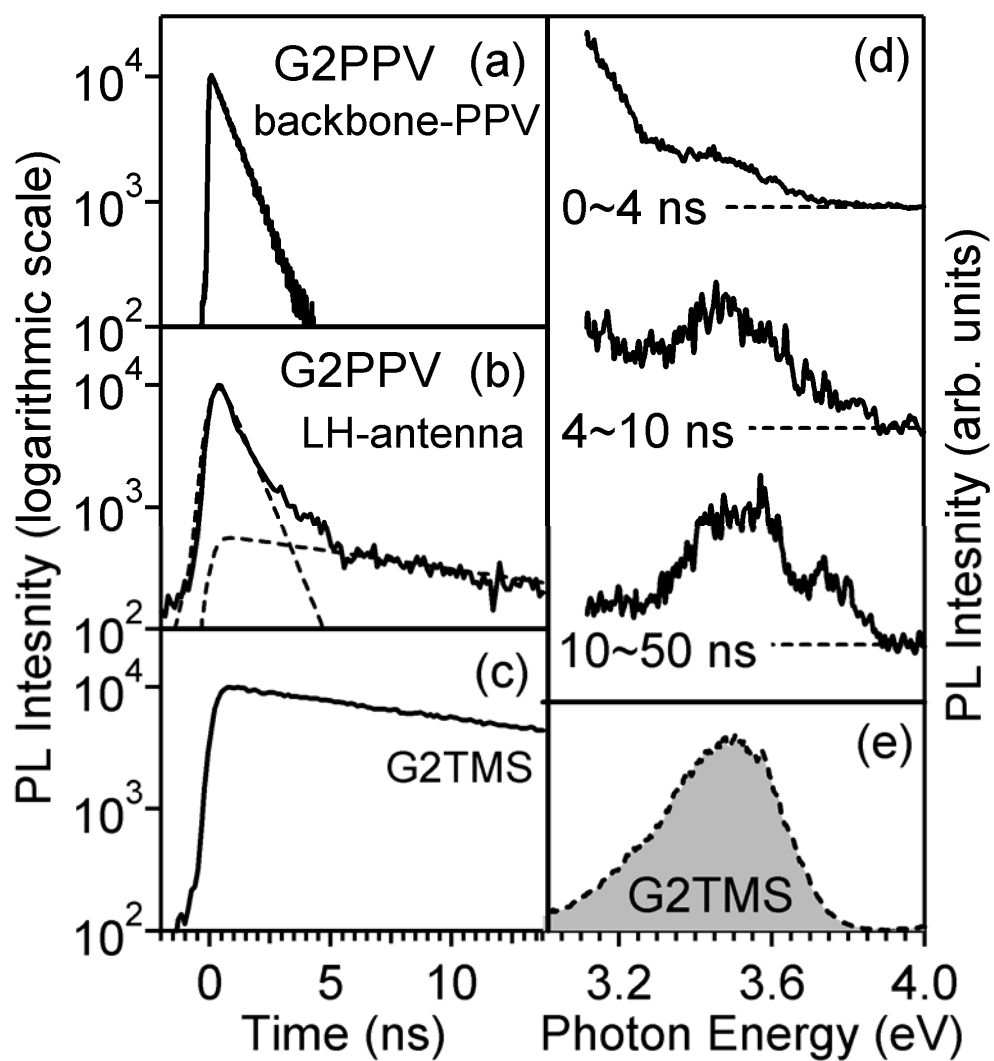


Fig.3

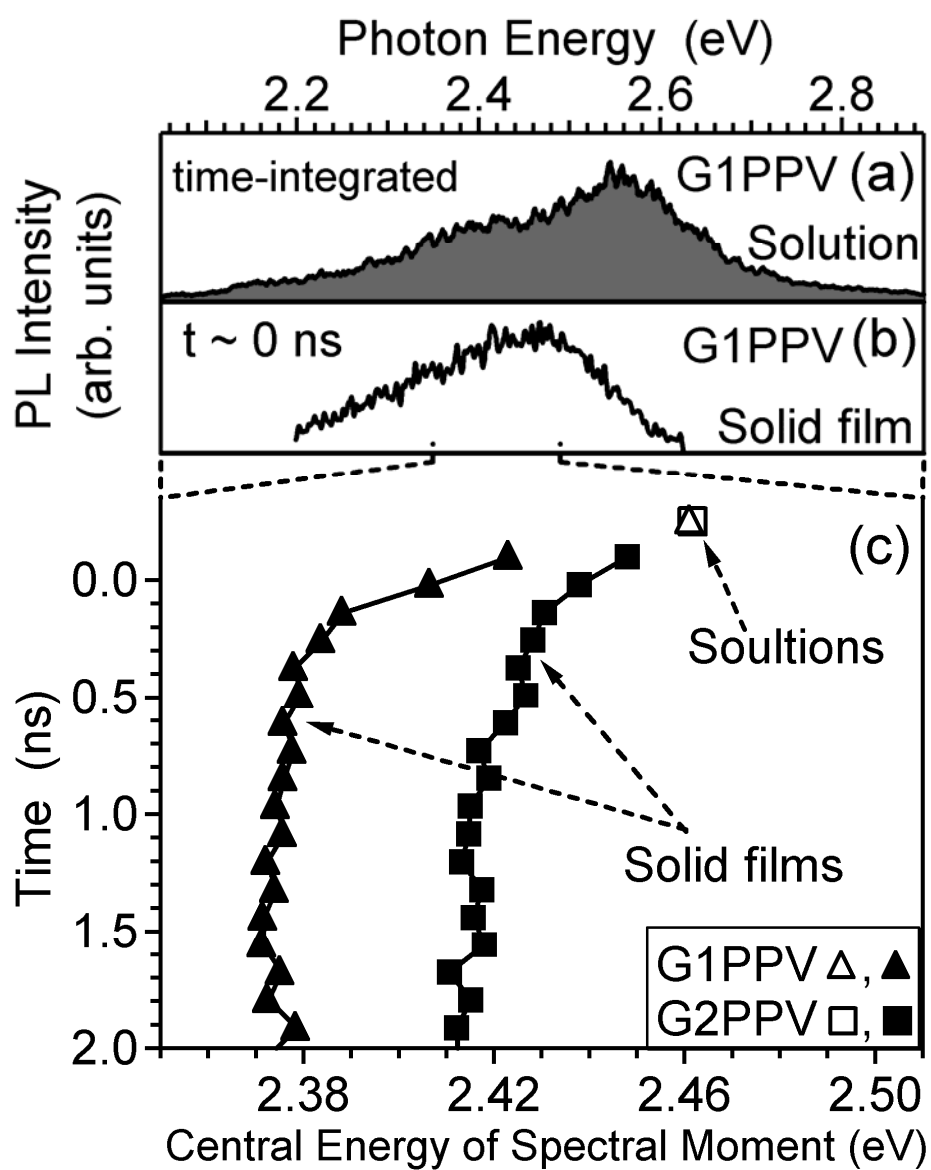


Fig.4